Standard Operating Procedure for the Extraction And Analysis of Pesticides in Fish

1.0 Scope and Application

1.1 This is a gas chromatographic (GC) method applicable for the extraction and determination for the listed analytes. This method is for the extraction of the analytes in fish tissue. This method should be used by, or under the supervision of experienced analysts. The analyst should be skilled in sonication extractions and use of GC, and interpretation of gas chromatograms.

1.2 This method is applicable to the determination of the target analytes over the ranges of 0.13 - 2.5µg/g. The method detection limits (MDLs) are determined by the standard concentrations and size of sample used.

1.3 The following compounds may require some special attention when being determined by this method:

1.3.1 Atrazine and g-BHC co-elute on the RTX-5 column. These compounds need to be analyzed by GC/MS for confirmation.

1.3.2 Endosulfan I and a-Chlordane co-elute on the column. These compounds need to be analyzed by GC/MS for confirmation.

1.3.3 Fenvalerate has multiple peaks. These peaks should be analyzed with care.

1.4 Target compounds that can be measured using this method include but are not limited to the following:

Analyte	CAS#
Ethalfluralin	55283-68-6
Trifluralin	1582-09-8
a-BHC	319-64-6
Triallate	2303-17-5
Diazinon	33-41-5
g-BHC (Lindane)	58-89-9
Atrazine	1912-24-9
Simazine	122-34-9
Heptachlor	76-44-8

b-BHC	319-85-7
d-BHC	319-86-8
Aldrin	309-00-02
Alachlor	15972-60-8
Chlorothalonil	1897-45-6
Methyl Parathion	298-00-0
Metolachlor	51218-45-2
Metribuzine	21087-64-9
Chlorpyrifos	2921-88-2
Dieldrin	60-57-1
Malathion	121-75-5
Ethyl Parathion	56-38-2
Heptachlor Epoxide	1024-57-3
Pendimethalin (Prowl)	40487-42-1
g-Chlordane	5103-74-2
trans-Nonachlor	39765-80-5
a-Chlordane	5103-71-9
Endosulfan I	959-98-8
DDE	72-55-9
Endosulfan II	33213-65-9
DDD	72-54-8
DDT	50-29-3
Endrin	72-20-8
Endrin Aldehyde	7421-93-4
Propoconazole (Tilt)	60207-90-1
Endosulfan Sulfate	1031-07-8
Methoxychlor	72-43-5
Endrin Ketone	53494-70-5
Fenvalerate	51630-58-1

2.0 Summary of Method

The analytes are extracted from the fish tissue in acetone by sonication. The extract is then filtered and analyzed by gas chromagraphy.

3.0 Definitions

The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

3.1 GC/ECD - gas chromatograph/electron capture detector

3.2 GC/MS - gas chroatograph/mass spectroscopy detector

3.3 Reagent water - Reagent water is defined as a water in which an interference is not observed above the EDL of each analyte of interest. A Millipore or Barnstead water system or its equivalent may be used to generate deionized reagent water. Distilled water that has been passed through granular charcoal may also be suitable. Reagent water is monitored through analysis of the laboratory reagent blank.

3.4 Quality Control Sample (QCS) - A solution of method analytes of known concentration which is used to fortify an aliquot of sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.5 Laboratory Fortified Blank (LFB) - A blank fish sample to which known quantities of the method anlaytes are added in the laboratory. The LFB is anlayzed exactly like a sample, and it purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.6 Laboratory Reagent Blank (LRB) - A blank fish sample that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.7 Laboratory Fortified Matrix (LFM) - Spiked Sample - An environmental sample to which known amounts of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM correct for background concentrations.

3.8 Laboratory Duplicate - Two aliquots LD1 and LD2 of the same sample designated as such in the laboratory. Each aliquot is extracted and analyzed separately with

identical procedures. Analysis of LD1 and LD2 indicate the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.9 Target Compound - An analyte or compound listed in section 1.4.

3.10 Surrogate Analyte - A pure analyte that is chemically similar to the target compounds but is not expected to occur in an environmental sample. It is added to a sample aliquot in a known amount before extraction and is measured with the sample procedures used to measure other sample components. The purpose of the surrogate is to monitor method performance with each sample.

3.11 Spiking Solution - A mixture of analytes listed in section 1.4. These compounds are added to the LFB and LFM in known amounts. The spiking solution is added before extraction to measure any effects of the matrix on the analytes and surrogates.

3.12 Stock Standard Solution (SSS) - A concentrated solution of one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.13 Primary Dilution Standard Solution - A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.14 Calibration Standards (CAL) - A solution prepared from the primary dilution standard solution and stock standards solutions of the internal standards and surrogate analysis. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.15 Continuing calibration check (CCC) - A calibration standard containing one or more method analytes which is analyzed periodically to verify the accuracy of the existing calibration curves or response factors for those analytes.

3.16 Tube spike and surrogate - Laboratory performance check sample - A solution of method analytes and surrogate in solvent that is used to evaluate the performance of the instrumental system with respect to a defined set of method criteria.

3.17 Method detection limit (MDL) - The MDL is defined as the minimum

concentration of an analyte that can be identified, measured, and reported with 99% confidence that the concentration is greater than zero.

3.18 Material Safety Data Sheet (MSDS) - Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire and reactivity data including storage, spill, and handling precautions.

3.19 MTBE - Methyl-tert-butyl-ether - Organic Solvent

3.20 Micrograms per gram (µg/g) - The final units for the concentration of the extracted analytes.

3.21 Definitions of a few terms in the method:

3.21.1 May: This action, activity, or procedural step is neither required nor prohibited

3.21.2 May not: This action, activity, or procedural step is prohibited.

3.21.3 Must: This action, activity, or procedural step is required.

3.21.4 Shall: This action, activity, or procedural step is required.

3.21.5 Should: This action, activity, or procedural step is suggested, but not required.

3.22 Estimated Detection Limit (EDL) - Defined as either the MDL or a level of a compound in a sample yielding a peak in the final extract that can be identified, measured, and reported with 99% confidence that the concentration is greater than zero.

3.23 MeCl - CH_2Cl_2 - Methylene Chloride - Dichloromethane - An organic solvent.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in chromatograms. All reagents and apparatus must be

routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks and described in section 9.3. Subtracting blank values from sample results is not permitted.

4.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by throughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with dilute acid, tap, and reagent water. Drain dry, and heat in an oven of muffle furnace at 400°C for 1 hour. Do not heat volumetric ware. Thermally stable materials such as PCBs might not be eliminated by this treatment. Thorough rinsing with acetone and hexane may be substituted for the heating. After drying and cooling, store glassware in a clean environment free of all potential contamination. To prevent any accumulation of dust or other contaminants, store glassware inverted or capped with aluminum foil.

4.2 The use of high purity reagents and solvents helps to minimize interference problems. Each new bottle of solvent should be analyzed before use. An interference free solvent is a solvent containing no peaks representing an concentration $\geq$ the MDL at the retention times of the analytes of interest. Purification of solvents by distillation in an all glass system may be required.

4.3 Matrix interferences may be caused by contaminations that are co-extracted from the sample, this will be higher with samples rich in organic matter. Analyte identification should be confirmed using the confirmation column or by MS.

4.4 Analytical bias may result from discrimination at the GC inlet. This can be minimized by optimizing the inlet configuration and injection technique.

4.5 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the ECD. These compounds generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalate, that are easily extracted or leached during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during exaction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalate can best be minimized by avoiding the use of plastic in the laboratory. Exhaustive purification of reagents and glassware may be required to eliminate background phthalate contamination.

4.6 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. Accordingly, exposure to these chemicals must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of MSDSs should also be made available to all personnel involved in the chemical analysis.

5.2 WARNING - When a solvent is purified, stabilizers added by the manufacturer are removed, thus potentially making the solvent hazardous.

6.0 Equipment and Supplies

Note: Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.1 Glassware

6.1.1 Clean glass containers with Teflon lined screw top (sample collection and storage of dried samples.)

6.1.2 200 - 250mL glass centrifuge bottles with Teflon lined screw top - 1 per sample.

6.1.3 Turbo Vap II collection tubes, 200mL maximum capacity - 1 per sample.

6.1.4 Hewlett Packard auto-sampler vials with Teflon lined tops.

6.1.5 Erlenmeyer flasks to be used to collect the filtered sample. May use one per sample or use one and rinse with acetone in between each sample.

6.1.6 Aspirated filter apparatus that can hold a 1µm filter. May use one and rinse with acetone in between samples or one per sample.

6.1.6.1 Filters that will fit into the filter apparatus that have a pore size of 1µm.

6.1.7 15mL graduated centrifuge tubes - 1 per sample.

6.2 Grinder - Capable of grinding the dried sample to a fine powder for homogenous sample for extraction.

6.3 Sonicator - Capable of holding all samples while in the 200mL centrifuge tubes.

6.4 Freeze Dryer - Capable of freeze drying the fish tissue sample for ease of sample handling during storage and extraction.

6.5 Balance - Analytical, capable of accurately weighing to the nearest 0.01g.

6.6 Zymarck Turbo Vap II or equivalent evaporation device.

6.7 Hewlett Packard 5890 Gas Chromatograph with data system.

6.7.1 The GC must capable of temperature programming and be equipped with a split/splitless injector.

6.7.2 GC supplies including injection port liners, ferrules, syringes, etc.

6.7.3 The gas chromatograph may be equipped with either an ECD or MSD.

6.7.4 An auto-injector is recommended for improved precision of analysis.

6.7.5 The interfaced data system is the LabSystems Xchrom or and equivalent system which allows for data acquisition, storage, retrieval, and calculations of results. (See manual for details)

6.7.6 Capillary column 30 meters long, 0.25mm ID, 0.25 micron film thickness or equivalent.

6.7.6.1 Primary column used in this method: Restek RTX-5ms an equivalent column may be used.

7.0 Reagents and Standards

7.1 Acetone, Hexane, and MTBE - Optima grade or nanograde or distilled in glass or in other words the highest purity to reduce any interference problems. The residue grade solvents are flammable and stored in an appropriate flammable storage area. Reagent grade inorganic chemicals shall be used in all tests.

7.2 Empore Filter Aid 400 or an equivalent filter aid.

7.3 Mirex - 99% purity, for use as surrogate standard. Available from a reputable chemical supply company.

7.3.1 20ug/mL solution is used as a surrogate. Prepare by weighing out an amount of solid into a 10mL volumetric flask and adding acetone to mark on flask. The resulting solution can be diluted to 20ug/mL. See figure 1 for an example of this dilution.

7.4 Reference Standards - Purchased from AccuStandard or equivalent. The calibration standards must be from a different source than the spiking solution. Stock standard solutions are stored in the vials in the organic lab refrigerator until read to be diluted to the calibration standards. Calibration standards should be checked frequently for signs of evaporation or degradation. Table 1 shows the concentrations of method analytes in the stock and calibration solutions.

7.5 Spiking Solution - Purchased from an reputable chemical supply company. The spiking solution must be from a different source than the references standards. Table 2 shows the concentration of the method analytes in spiking solution.

7.6 Hydrochloric acid (HCl) for rinsing glassware:

7.6.1 400mL concentrated HCl in 4L reagent water.

8.0 Sample Collection, preservation, and storage

8.1 Fish samples may be collected, cut or ground, and frozen in clean glass containers with Teflon lined screw tops.

8.2 Place the wet frozen sample into the freeze dryer containers. Allow the samples to be freeze dried according to machine instructions.

8.3 Place the dried samples into the grinder and grind samples to a homogenous mixture. The grinder must be cleaned between samples to prevent cross contamination of samples.

8.4 Store the dried and ground samples in clean glass containers with Teflon lined screw tops. The samples may be stored at room temperature. There is no set hold time for the samples before extraction. The extracts should only be held for a maximum of 14 days before analysis.

9.0 Quality Control

9.1 Minimum quality control (QC) requirements are an initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, analytes of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples.

9.2 The analyst is permitted to modify the GC columns, GC conditions, detectors, continuous extraction techniques, concentration techniques, internal standards or surrogate compounds.

9.3 Laboratory reagent blanks (LRB) - Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If within the retention time window of any analyte the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

9.4 Assessing laboratory performance - Laboratory Fortified Blank (LFB)

9.4.1 The laboratory must analyze at least one LFB sample with every sample set. The concentration of each analyte should be 10 times the EDL.

Calculate accuracy as percent recovery.

9.4.2 The control limits are set values as follows:
Upper Control Limit = 150%
Lower Control Limit = 50%

9.2.3 It is recommended that the laboratory periodically determine and document its detection limit capabilities for the analytes of interest.

9.5 Laboratory Fortified Sample Matrix - Spike Sample

9.5.1 The laboratory must add the spiking solution to a minimum of one sample per sample set.

9.5.2 Calculate the percent recovery, P, of the concentration for each analyte, after correcting the analytical result, X, from the fortified sample for the background concentration, b, measured in the unfortified sample.

$$P = 100(X-b)/\text{fortifying concentration}$$

9.5.3 If the recovery of any such analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Sec. 9.4), the recovery problems encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effect.

9.6 Assessing instrument system - Laboratory performance check sample - Instrument performance should be monitored on a daily basis by analysis of the LPC sample. The LPC sample contains compounds designed to indicate appropriate instrument sensitivity, column performance and chromatographic performance. Inability to demonstrate acceptable instrument performance indicated the need for reevaluation of the instrument system.

10.0 Calibration and Standardization

10.1 Establish GC operating parameters equivalent to those indicated in Sect. 6.7 and Table 3. The system should be calibrated using the following techniques. NOTE: Calibration standard solutions must be prepared such that no unresolved analytes are mixed together.

10.2 External Calibration

10.2.1 Prepare calibration standards at a minimum of three concentration levels for each analyte and surrogate compound. Table 1 shows how to prepare the standards. The lowest standard should represent analyte concentrations at the EDL. The remaining standards should bracket the analyte concentrations expected in the samples and should define the working range of the detector.

10.2.2 Starting with the standard of lowest concentration, analyze each calibration standard according to section 11.5 and tabulate response area versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. The chromatography data system software may be used to establish the calibration curve.

10.2.3 The working calibration curve must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day.

10.2.4 Single point calibration is a viable alternative to a calibration curve. Prepare a single point standard at a concentration that produces a response that deviated from the sample extract response by no more than 20%.

10.2.5 Verify calibration standards periodically by analyzing a standard prepared from reference material obtained from an independent source.

11.0 Procedure

11.1 Preparation

11.1.1 Weigh 2 grams ($\pm$ 0.05g) of dried and ground sample into 200mL centrifuge bottles. Include one LRB, LFB, matrix sample spike, and sample duplicate.

11.1.2 Fortify each sample with 50µL 20µL Mirex surrogate.

11.1.3 Spike the LFB, and sample spike with 100µL of spiking solution, see table 2 for concentration of analytes.

11.2 Extraction

11.2.1 Add 100mL acetone to each sample. Seal and shake to mix.

11.2.2 Sonicate the sealed samples in a lab sonicator for 1 hour. NOTE: Shake the samples periodically to break the bead of sample in the container to aid in the extraction.

11.3 Clean up, Solvent exchange, and final volume adjustment

11.3.1 Filter each sonciated sample through a 1µm filter paper. Use the aspirated filter apparatus to pull the sample through the paper. Filter aid may be placed on the filter paper to assist in the filtering. NOTE: Rinse the filter apparatus with acetone between each sample to avoid cross contamination.

11.3.2 Transfer each filtered sample to a clean Turbo Vap II concentrator tube. Rinse the collection flask 3 times with acetone and transfer each rinsing to the concentrator tube.

11.3.3 Evaporate the extracts to about 1mL using the turbo vap and rinse the inner sides of the turbo vap evaporation vessel with MTBE.

11.3.4 Repeat evaporation and rinsing with MTBE for a total of 3 times. The solvent of the extracts in now MTBE.

11.3.5 Quantitatively transfer solvent exchanged extracts to clean 15mL graduated centrifuge tubes. Adjust the final volume of each sample to 5mL.

11.3.6 Make up LPC samples. To an aliquot of 5mL MTBE add the same concentration of Mirex and method analytes. See Section 11.1 for amounts.

11.3.7 Transfer about 1mL of sample to autosampler vials, seal, and analyze by GC/ECD or GC/MS.

11.4 Gas Chromatography

11.4.1 Section 6.7 summarizes the recommended operating conditions for the GC. Included in table 3 are retention times observed using this method. Other

GC columns, chromatographic conditions, or detectors may be used.

11.4.2 Calibrate the system daily as described in section 10.0. The standards and extracts must be in MTBE.

11.4.3 Inject 1µL of the sample extract. Record the resulting peak size in area units and the retention times of the peaks. The chromatography data system may be used to record data.

11.4.4 If the response for the peaks exceeds the response for the highest concentration calibration standard, dilute the extract and re-analyze

11.5 Identification of anlaytes

11.5.1 Identify a sample component by comparison of its retention time to the retention times of components in the standard chromatogram. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound, then the identification is considered positive.

11.5.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5.3 True identification of the analytes requires confirmation on a dissimilar column or by GC/MS.

12.0 Calculations and reporting results

The chromatography data system software may be used to calculate the results instead of the manual calculations shown below.

12.1 Calculate analyte concnetration in the sample from the response for the analyte using the calibration proceedure described in section 10.

12.2 Calculate the amount of material injected from the peak response using the calibration curve determined in section 10.2. The concentration (C) in the sample can be calculated from the following equation.

$$C(\mu g/L) = \frac{(A)(V_t)}{(V_i)(1000)}$$

A = Amount of material injected (ng) (found from calibration curve)
V_i = Volume of extract injected (µL) (1µL)
V_t = Volume of total extract (µL) (5mL = 5000)

12.3 Values for each analyte should be reported in µg/g. To calculate this use the following equation:

$$R(\mu g/g) = C(\mu g/L) / Wi$$

R = Concentration of analyte in µg/g
C = Concentration calculated in 12.2 (µg/L)
Wi = Weight of solid sample used in 11.1.1 (g)

12.3 The results for each analyte should be reported in µg/g as per a dry weight basis.

13.0 Method Performance

There is data to show that this method is accurate and precise. Table 4 shows some results for this method.

14.0 Pollution Prevention

The large volume of organic solvent is a potential for pollution. The analyst should take care to properly use the solvent in vented hoods. The excess solvent can be placed in hoods to evaporate or can be recycled or disposed of in an environmentally sound manner according to local regulations.

15.0 Waste Management

15.1 The volume of organic solvent should have a plan of action for waste management. The fish sample can be disposed in the garbage, and the organic solvent can be recycled or evaporated into a vented hood.

15.2 For further information on waste management consult The Waste Management Manual for Laboratory Personnel and Less is Better: Laboratory Chemical Management of Waste Reduction, both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

16.0 References

17.0 Tables and figures

Figure 1. Example of calculations of Mirex dilution.

Weight of empty 10mL volumetric Flask	15.456g
Weight of volumetric flask and mirex solid	15.4805g
Weight of mirex solid used	0.0245g
Weight of mirex in mg	0.0245g x 1000 = 24.5mg
Weight of mirex in µg	24.5mg x 1000 = 24500µg
Concentration of mirex µg/ml	24500ug / 10mL = 2450µg/mL

Dilution to 20µg/mL

816µL (2450µg/mL) into 100mL volumetric flask = 20µg/mL

Table 1: Calibration Standard Concentration and Preparation

Concentration for each analyte in Calibration Standards

Analyte	Stock Solution	Std 1 µg/ml	Std 2 µg/ml	Std 3 µg/ml	Std 4 µg/ml	Std 5 µg/ml	Std 6 µg/ml
All Analytes	10µg/mL	0.05	0.10	0.25	0.5	1.0	2.5
Mirex	20µg/mL	0.2	0.2	0.2	0.2	0.2	0.2

All standards are made up by dilution of the stock solution to 1mL
As follows:

Standard	Amount of MTBE (µL)	Amount of Stock Solution (µL)	Amount of Mirex (µL)
1	985	5	10
2	980	10	10
3	965	25	10
4	940	50	10

5	890	100	10
6	740	250	10

Table 2: Concentration of Analytes in Spiking Solution

Concentration of All Analytes in Spiking Solution: 10µg/ml

Table 3: Guide to Retention Times

Injector @ 200ºC, ECD detector at 300ºC
Oven Program: Hold at 90ºC for 1 minute
Ramp to 300ºC at 3ºC/min, hold 5 minutes
Retention time and order found on the GC/ECD column
NOTE: these times and order are meant to be a guide only.

Analyte	Retention Time	Analyte	Retention Time
Ethalfluralin	25.21	d-BHC	37.65
Trifluralin	25.38	Aldrin	37.80
a-BHC	30.74	Alachlor	37.93
Triallate	33.37	Methyl Parathion	39.97
Diazinon	33.78	Metolachlor	40.02
Atrazine	33.88	Metribuzine	40.29
g-BHC	33.88	Chlorpyrifos	41.11
Simazine	34.45	Malathion	41.76
Heptachlor	35.68	Ethyl Parathion	41.99
b-BHC	36.17	Hept.. Epoxide B	42.21

Pendimethalin	42.92	g-Chlordane	43.46
Trans-Nonachlor	43.79	a-Chlordane	44.46
Endosulfan I	44.46	Cyanazine	45.14
DDE	46.43	Dieldrin	46.67
Endrin	48.84	DDD	50.34
Endosulfan II	50.67	DDT	52.09
Endrin Aldehyde	52.77	Endosulfan Sulfate	53.81
Mirex	57.23	Methoxychlor	57.89
Endrin Ketone	57.97	Fenvalerate	68.37

Table 4: Method Performance

Analyte Accuracy and Precision Data[1]

Analyte	Fortified Conc (µg/L)	Mean Meas Conc (µg/L)	std dev (µg/L) %	EDL[2] (µg/L)	EDL[3] (µg/g)
Ethalfluralin	1.0	0.99	0.23	0.25	0.13
Trifluralin	1.0	1.01	0.25	0.25	0.13
a-BHC	1.0	0.96	0.25	0.25	0.13
Triallate	1.0	0.94	0.17	0.25	0.13
Diazinon	1.0	1.11	0.81	0.25	0.13
g-BHC	1.0	1.10	0.70	0.25	0.13
Simazine	1.0	18.43	23.92	0.25	0.13
Heptachlor	1.0	0.92	0.22	0.25	0.13

[1]Produced by analysis of ??? fortified soil samples

[2]Estimate detection limit

[3]Estimated detection limit EDL(µg/L)/2g = EDL (µg/g)

b-BHC	1.0	0.72	0.32	0.25	0.13
d-BHC	1.0	0.98	0.75	0.25	0.13
Aldrin	1.0	0.56	0.36	0.25	0.13
Alachlor	1.0	0.94	0.24	0.25	0.13
Chlorothalonil	1.0	1.23	1.44	0.25	0.13
Methyl Parathion	1.0	1.05	0.26	0.25	0.13
Metolachlor	1.0	0.91	1.11	0.25	0.13
Metribuzine	1.0	0.98	0.27	0.25	0.13
Chlorpyrifos	1.0	0.85	0.23	0.25	0.13
Malathion	1.0	1.10	0.36	0.25	0.13
Analyte	Fortified conc	Mean Meas Conc	Std Dev	EDL (µg/L)	EDL (µg/g)
Ethyl Parathion	1.0	0.88	0.22	0.25	0.13
Heptachlor epoxide	1.0	0.83	0.19	0.25	0.13
Pendimethalin	1.0	0.83	0.18	0.25	0.13
g-Chlordane	1.0	0.86	0.19	0.25	0.13
trans-Nonachlor	1.0	0.86	0.19	0.25	0.13
a-Chlordane	1.0	0.77	0.19	0.25	0.13
DDE	1.0	0.82	0.17	0.25	0.13
Dieldrin	1.0	0.90	0.22	0.25	0.13
Endrin	1.0	0.89	0.19	0.25	0.13
DDD	1.0	0.90	0.21	0.25	0.13
Endosulfan II	1.0	0.86	0.2	0.25	0.13
DDT	1.0	1.35	0.45	0.25	0.13
Endrin Aldehyde	1.0	0.38	0.27	0.25	0.13

Endosulfan Sulfate	1.0	1.03	0.44	0.25	0.13
Mirex	1.0	2.0	2.52	1.0	0.5
Methoxychlor	1.0	1.26	0.47	0.25	0.13
Endrin Ketone	1.0	1.10	0.28	0.25	0.13
Fenvalerate	1.0	1.20	0.4	0.25	0.13